



Highly selective rearrangement of furfuryl alcohol to cyclopentanone



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ABSTRACT

The aqueous phase hydrogenation of furfuryl alcohol to cyclopentanone was carried out on a series of metal supported and bulk catalysts. The effect of catalyst concentration, temperature, hydrogen pressure and reaction time has also been investigated. By changing the partial hydrogen pressure and concentration of metal catalyst it is possible to transform furfuryl alcohol with a very high selectivity either to furfuryl alcohol or cyclopentanone. High hydrogen pressure and catalyst concentration favours the formation of tetrahydrofurfuryl alcohol. At very low concentration of metal catalyst (0.25–1.0 wt%) and 0.8–2.5 MPa of hydrogen pressure, the product is exclusively cyclopentanone formed in yields higher than 95 mol%. Very active and selective are nickel type catalysts. The differences in selectivities of products distribution are explained by the proposed reaction mechanism consisting of two parallel reactions. One reaction is catalyzed preferably by hydrogen ions produced by self-dissociation of water and other by metal catalyst.

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1. Introduction

In the past years the production of chemicals from biomass has received increased attention in view of the replacement of petroleum. Furfural is one of basic chemicals obtained from hemi-cellulose raw material via acid-catalyzed dehydration [1–7]. Gas or liquid-phase hydrogenation of multifunctional furfural (FA) over heterogeneous catalysts can produce various useful products described recently in overviews by Nakagawa et al. [8] and Gallezot [9].

Selective hydrogenation of the C=O bond of furfural leads to an industrially important chemical, furfuryl alcohol (FAL), which is applied mostly in polymer industry for the production of corrosion and acid-resistant materials. Subsequent hydrogenation of the C=C bonds of furfuryl alcohol gives tetrahydrofurfuryl alcohol (THFA), usually used as a green solvent. Nickel based catalysts [10,11] and noble metals [12,13] are generally applied for this reaction in a liquid phase. Recently, we have reported [14] that in water as a solvent furfural and furfuryl alcohol in the presence of heterogeneous Pt, Pd, Ru, Ni catalysts are at higher temperatures and hydrogen pressures selectively converted to cyclopentanone. Under these conditions and in the absence of metal catalysts the main products of furfuryl alcohol conversion in water are 4-hydroxy-2-cyclopentenone (4-HCP) and polymers of furfuryl alcohol [15]. These products are result of acid-catalyzed ring-rearrangement reaction of furfuryl

alcohol and its polymerization. Acid catalyst (H_3O^+) is formed by self-dissociation of water serving as the solvent.

Cyclopentanone is a versatile compound used for the synthesis of fungicides, pharmaceuticals, rubber chemicals, and flavour and fragrance chemicals [16]. Potentially, it can be used for preparation of polyamides [17] and C_{15} – C_{17} diesel or jet fuels [18]. Cyclopentanone can be prepared by the catalytic vapour-phase cyclisation of 1,6-hexanediol [19] or adipic esters [20–22] or by the liquid phase oxidation of cyclopentene with nitrous oxide [23,24]. In all these processes petroleum-based products are used as feed stocks.

In this paper, we report how we can principally change the selectivity of furfuryl alcohol conversion in water either to tetrahydrofurfuryl alcohol or to cyclopentanone by varying the hydrogen pressure or concentration of metal catalyst. The knowledge of this dependence offers us the possibility to achieve very high yields of cyclopentanone directly from furfuryl alcohol at very low catalyst concentrations and hydrogen pressures. To the best of our knowledge, no available literature describes such highly selective conversion of furfuryl alcohol to cyclopentanone under comparable concentration and reaction conditions.

2. Materials and methods

2.1. Materials

Furfuryl alcohol (98%), tetrahydrofurfuryl alcohol (99%), cyclopentanone (99%) and cyclopentanol (99%) were purchased from Sigma–Aldrich, and were used without purification. Pt, Pd

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and Ru catalysts with 5 wt% of metal on activated carbon powder were purchased from Johnson Matthey Co. The nickel catalysts G-134, G-49 and NiSat® 320 RS were purchased from Sud Chemie and catalyst Actimet C from BASF. Supported nickel catalysts were prepared by incipient wetness impregnation of powdered (particle sizes < 110 µm) activated charcoal Norit (Fluka) and SiO₂ Sylobloc 46 (surface area 306 m² g⁻¹, Grace Davison) with aqueous solutions of nickel nitrate. The concentration of solutions was settled in order to obtain nominal metal loadings of 5 and 10 wt%, respectively. After drying at 100 °C for 6 h solids were reduced in hydrogen at 500 °C for 2 h. The prepared nickel catalysts had average metal particle size determined from XRD data 13.5 and 15.7 nm, respectively. The mixed oxide Ni–Mg–Al catalyst with molar ratio of metals 1:1:1 in fresh catalyst was prepared using the coprecipitation method [25]. As the precipitant was added dropwise 4% NH₄OH to an aqueous solution containing an appropriate amount of Ni(NO₃)₂, Al(NO₃)₃ and Mg(NO₃)₂. The solution was stirred at 40 °C until the pH reached 8.0. The precipitate was separated by a centrifuge, and then dried at 110 °C overnight and calcined at 650 °C for 5 h. Before reaction, the precursor was grinded and sieved to 75–110 µm, and reduced at 500 °C in hydrogen atmosphere for 3 h.

2.2. Catalytic tests

Catalytic experiments were performed using procedure and analytical methods described in our previous paper [26]. For a typical reaction 20 ml of water, 1.0 g of furfuryl alcohol and a given amount of metal catalyst were loaded into the reactor vessel. After sealing, the reactor was several times flushed with low pressure hydrogen and then pressurized with hydrogen usually to 0.8–2.5 MPa (ambient temperature). The reactor was then heated to the desired temperature and the stirring speed fixed to 1500 rpm to eliminate the diffusion effects. After an appropriate reaction time the reactor was quickly cooled down, the reactor contents poured out to vial and the catalyst separated from the aqueous phase by centrifugation. The aqueous phase was analyzed using gas chromatography (Hewlett Packard 5890 Series II, with FID detector). The quantitative determination of the reaction products was done by the external standard method using aqueous solutions of each product with known concentration and response factor. A gas chromatograph–mass spectrometer combination (GC/MS QP 5000 Shimadzu with HP-1, 50 mm × 0.2 mm capillary column) was used to identify the organic compounds. Prior to GC/MS analysis, the aqueous phase saturated with NaCl was several times extracted with dichloromethane. The composition of the gas phase was determined using gas chromatography (Shimadzu GC-17A equipped with TC and FID detectors). We found only trace amounts of carbon oxides, methanol and light hydrocarbons in the gas phase. FAL conversion (X_{FAL}), yield (Y_i) and selectivity of product i (S_i) were calculated as follows:

$$X_{\text{FAL}} = \frac{n_{\text{FAL}}^0 - n_{\text{FAL}}}{n_{\text{FAL}}^0} \times 100\%$$

$$Y_i = \frac{n_i}{n_{\text{FAL}}^0} \times 100\%$$

$$S_i = \frac{Y_i}{X_{\text{FAL}}} \times 100\%$$

where i represents mol of the corresponding product, and n_{FAL}^0 and n_{FAL} depict the mol of FAL in the reaction mixture before and after reaction, respectively.

3. Results and discussion

The study of the influence of reaction parameters on the hydrogenation of furfuryl alcohol in water as a solvent has shown, that crucial parameters affecting the selectivity to the main reaction products are concentration of the heterogeneous metal catalyst (Fig. 1) and partial pressure of hydrogen (Fig. 2). These data were obtained at an impeller speed of 1500 rpm, which ensured that in the given volume of reaction mixture the gas–liquid and liquid–solid mass-transfer resistance can be ignored. The catalyst particle size was varied to test the significance of intra-particle mass-transfer resistance. Two experiments were carried out at 160 °C and 2.5 MPa of hydrogen using catalyst particle sizes < 75 µm and in the range between 75 and 110 µm, respectively. It was found that in these ranges the metal catalyst particle size had no effect on the yields of two main reaction products, cyclopentanone and tetrahydrofurfuryl alcohol. From these results it is seen that the mass-transfer resistances do not influence the distribution of the main reaction products.

The observed differences in selectivities depicted in Figs. 1 and 2 are apparently related to the mechanism of conversion of furfuryl alcohol in water as a solvent. As we have found ([15] and Table 1, Run 1) in nitrogen or hydrogen atmosphere at temperatures above 110 °C furfuryl alcohol dissolved in pure water is by the furan ring-rearrangement reaction rapidly converted to 4-hydroxy-2-cyclopentenone and by parallel reaction to condensation products and polymers (Scheme 1). These reactions are catalyzed by hydrogen ions formed by auto-dissociation of water. However, if in the similar reaction system is present also the hydrogenation catalyst

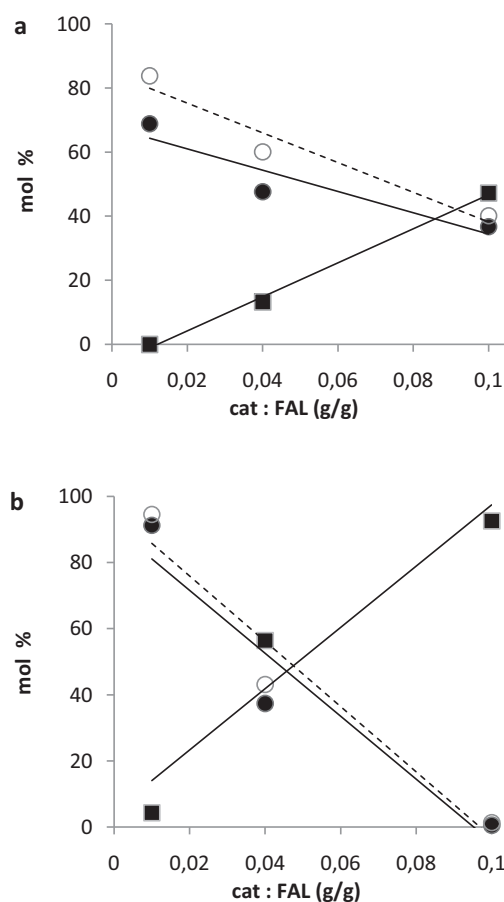


Fig. 1. Effect of catalyst concentration on the yield of THFA (■), CPON (●) and the sum of CPON + CEON (○) at partial hydrogen pressure (a) 0.8 MPa and (b) 2.5 MPa. Conditions: 1.0 g FAL; 20 g H₂O; 160 °C; reaction time: 60 min; nickel catalyst G-134

Table 1Conversion of furfuryl alcohol in water (conditions: 160 °C; 20 ml H₂O, reaction time 60 min; catalyst G-134).

Run	Catalyst (g)	Additive (g)	P_{H_2} (MPa)	Conversion (%)	Yield (mol%)				TOF ^d (s ^{−1})
					C _{PON}	C _{POL}	CEON	THFA	
1	No	–	0.8 ^a	98.7	54.4 ^b	–	–	–	–
2	0.1	–	2.5 ^a	100	57.1 ^b	–	–	–	–
3	0.04	–	2.5	100	23.5	3.4	0	67.3	0.19
4 ^c	0.01	–	2.5	0	0	0	0	98.7	–
5	0.04	–	0.8	100	41.6	0.7	19.0	15.3	0.34
6	0.04	0.05 g AcOH	0.8	100	88.5	1.6	0	1.4	0.73
7	0.01	–	0.8	100	68.9	0.9	14.1	0	2.28
8	0.01	0.05 g AcOH	0.8	100	75.8	0.7	2.2	1.9	2.51
9	0.01	0.02 g NaOH	0.8	42.6	17.0	0.5	0	23.0	0.56

C_{PON} cyclopentanone; FAL furfuryl alcohol; CEON 2-cyclopentenone; THFA tetrahydrofurfuryl alcohol; AcOH acetic acid.^a Nitrogen atmosphere;^b Yield of 4-HCP and the rest to 100% are polymers.^c THFA.^d Turnover frequency in grams of cyclopentanone produced per gram of catalyst per second.

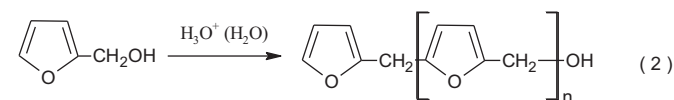
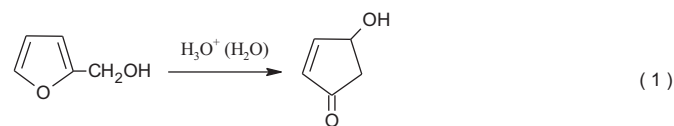
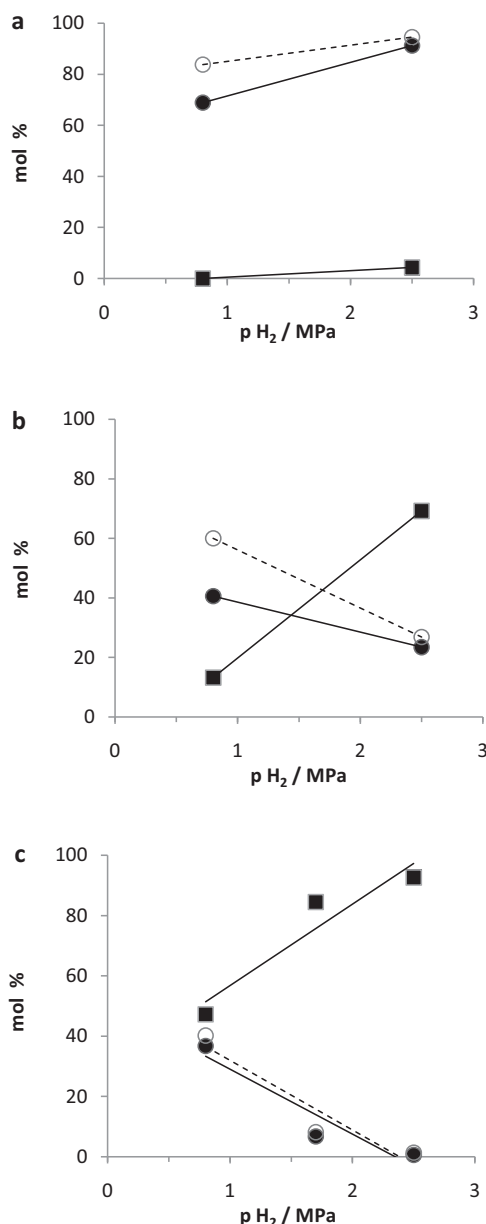
and a sufficient concentration of hydrogen dissolved in the liquid phase (i.e., according to the Raoult's law a sufficient partial pressure of hydrogen) furfuryl alcohol is hydrogenated to tetrahydrofurfuryl alcohol or converted to cyclopentanone (Scheme 2).

The experimentally observed strong dependence of products distribution on catalyst concentration and the partial pressure of hydrogen (Figs. 1 and 2) can be explained considering that in water furfuryl alcohol is converted to the mentioned reaction products through two catalytically different reaction pathways which proceed simultaneously. One reaction pathway catalysed by metals (reaction (3)) is hydrogenation of FAL to THFA, and the parallel pathway is an irreversible rearrangement reaction of furfuryl alcohol to cyclopentanone precursors (reaction (4)) catalysed by hydrogen ions formed by auto-dissociation of water.

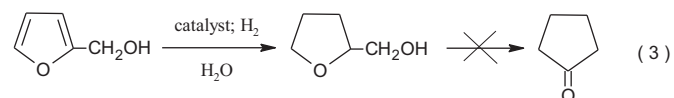
Thus, under sufficient gas–liquid interface areas and very low concentrations of metal catalyst (catalyst/FAL weight ratio 0.01) the rate of FAL hydrogenation to tetrahydrofurfuryl alcohol (reaction (3)) is in the range of partial hydrogen pressures 0.8–2.5 MPa very slow and the dominant reaction is the furan-ring rearrangement leading to the intermediate species (*) of cyclopentanone formation (reaction (4)). The impact of metal catalyst concentration and hydrogen pressure on the rate of reaction (4) is low, because the rate of this acid-catalysed reaction is influenced by the concentration of hydrogen ions. The concentration of hydrogen ions is dependent on the dissociation constant of water [27], i.e. at the constant reaction temperature it is the same. Separate experiments in an inert atmosphere at 160 °C have shown (Table 1, Run 2), that the presence of the nickel catalyst in the reaction medium in concentration 0.1 g catalyst per gram of FAL practically does not influence the conversion of FAL to 4-HCP, which is catalysed by hydrogen ions [15]. It means that at constant hydrogen pressure and FAL concentration according to Scheme 2, increasing concentration of metal catalyst enhances mainly the rates of reactions (3), (5) and (6) which are catalysed by metals. Reaction (3) leads to tetrahydrofurfuryl alcohol as the product. At very low concentration of metal catalyst and partial pressures of hydrogen 0.8 or 2.5 MPa the reaction product is exclusively cyclopentanone produced in yields higher than 90 mol%. The hydrogenation of the double bonds of furan ring into THFA is relatively low (Fig. 2a). The yield of THFA increases from 0.3 to 7.1 mol% at 0.8 and 2.5 MPa H₂, respectively. On the other hand the intermediate product, 2-cyclopentenone which is at 0.8 MPa of hydrogen formed by reaction (5) in about 15 mol% yield is through reaction (6) completely hydrogenated to cyclopentanone at 2.5 MPa of hydrogen. In all experiments depicted in the figures, the conversion of furfuryl alcohol was higher than 98.5% and cyclopentanol was formed only in 0.5–2.5 mol% yields.

From the kinetics of reactions (3) and (4) follows that the rate of metal catalysed reaction (3) should be significantly influenced by the concentration of hydrogen in the liquid phase. In addition, some impact on this rate can also have the structure and the size of metal particles of the heterogeneous catalyst. This effect was observed for Ni/SiO₂ catalysts in gas-phase hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol [28]. Since the rate of reaction (4) is preferably determined by the concentration of hydrogen ions but not by the metal catalyst, due to the selectivity towards cyclopentanone given by the ratio of the rates of reactions (4) and (3) it must decline with the rise of hydrogen pressure. As is seen from Fig. 1 and Fig. 2 at high hydrogen pressures (about 2.5 MPa) and high catalyst concentration (0.1 g catalyst/1 g FAL) the product of FAL conversion was exclusively tetrahydrofurfuryl alcohol. On the other hand, if the experiments were conducted in the presence of very low concentration (0.01 g catalyst per gram FAL) of nickel catalyst (Fig. 2a) the effect of hydrogen pressure on the conversion of FAL to cyclopentanone and THFA was small. The last mentioned results also indicates that under these reaction conditions the rate of consecutive hydrogenation of the primary intermediate species (*) to 2-cyclopentenone (reaction (5)), is more rapid than the rate of reaction (3). In experiments performed at low catalyst concentrations and hydrogen pressures about 14–19 mol% of 2-cyclopentenone was detected in the reaction mixtures (Table 1, Runs 5 and 7). This intermediate product is formed in larger amounts in the first minutes of reaction but by prolongation of reaction time it is completely hydrogenated to cyclopentanone (Fig. 3). Since the reaction (4) is irreversible it suggests that under these conditions, the rate of reaction (6), i.e. the hydrogenation of 2-cyclopentenone to cyclopentanone is the rate determining step. The higher rate of this reaction can be achieved by increasing hydrogen pressure and catalyst concentration. However, these parameters have a negative impact on the selectivity to cyclopentanone; they increase the rate of parallel reaction, i.e. the hydrogenation of FAL to THFA.

2-Cyclopentenone is the product of transformation of primary intermediate species (*) formed during furfuryl alcohol rearrangement. The rearrangement reaction starts with the attack of the OH group of FAL with the hydrogen ion. In the literature are proposed several reaction mechanisms of rearrangement of furfuryl alcohol derivatives (but in the absence of metal catalyst and hydrogen) which deliver functionalised cyclopentenones [29–33]. In the proposed rearrangement mechanisms are formed through cascade reactions involving ring opening and intramolecular condensation reaction steps intermediates like diketones, formylketones, zwitterionic species which after cyclisation gave functionalised cyclopentenones. However, despite large number of studies the examples describing the rearrangement

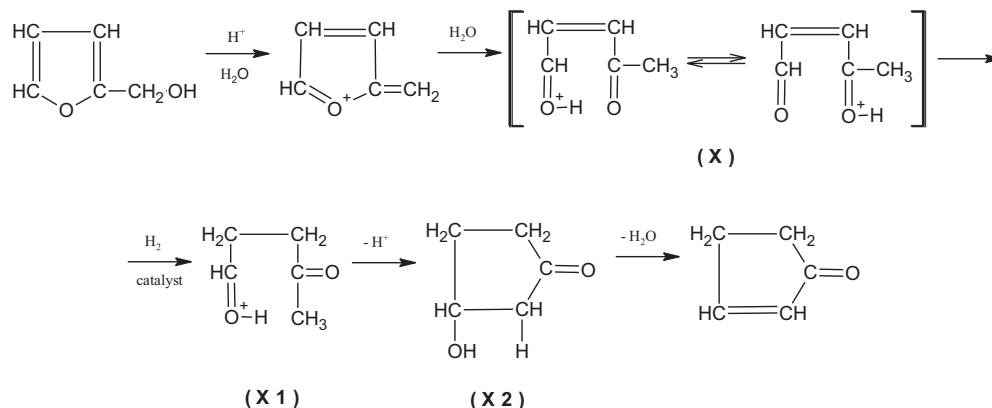


Scheme 1. Reaction pathways of furfuryl alcohol reaction in water in nitrogen or hydrogen atmosphere in the absence of metal catalyst.



Scheme 2. Reaction pathways of furfuryl alcohol transformation in water. (*) denotes intermediate species of furan ring rearrangement.

of furfuryl alcohol alone are very rare [15,34]. The stable product of this acid-catalyzed reaction is 4-HCP, which in pure water and an inert atmosphere is at higher temperatures formed in the yields higher than 45 mol%. Simultaneously with this product are formed yellow or red-brown coloured water insoluble polymers (Scheme 1). Similar results were obtained in hydrogen atmosphere but in the absence of metal catalyst (Table 1, Run 2). However, when the last mentioned reaction was conducted under 0.8 MPa of hydrogen pressure and even in the presence of very low nickel catalyst concentration (about 0.01 g per gram of FAL) the reaction mixture remained homogeneous without the presence of typical coloured solid polymers, and the major products were cyclopentanone and THFA. Using the GC/MS technique, in the reaction mixture was detected only small amount



Scheme 3. Possible pathway for the formation of cyclopentenone. The intermediate species are stabilized on metal surface.

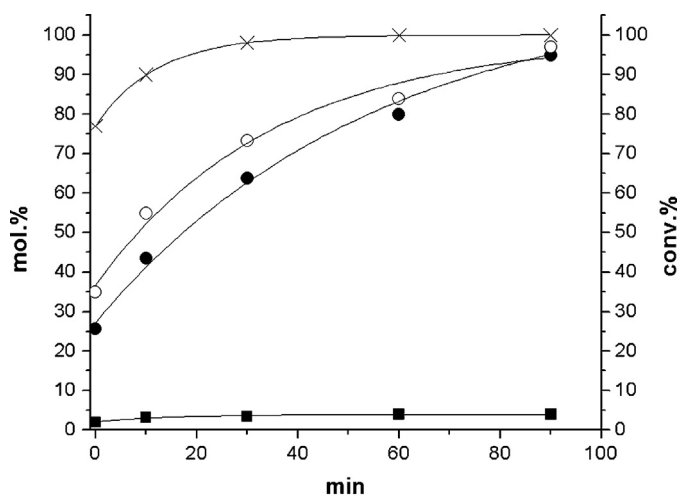


Fig. 3. Time dependence of FAL conversion (+) and the yield of C_{PON} (●), the sum of C_{PON} + C_{CEON} (○) and THFA (■). Conditions: 160 °C; weight ratio catalyst:FAL = 0.01; 0.8 MPa H₂.

of 4-HCP. In the most reaction mixtures of FAL hydrogenation 4-HCP was not present. The explanation for the absence of 4-HCP in the reaction mixtures might be that the rate of its dehydration/hydrogenation towards 2-cyclopentenone is under reaction conditions very high. Acidic media should enhance the dehydration reaction of intermediate 4-HCP. Therefore, not only the metal catalyst but probably also hydrogen ions from dissociation of water may enhance the conversion of 4-HCP. It is important to note that in many reaction mixtures of this study beside 4-HCP were by GC/MS determined in low concentrations various compounds containing one or more hydroxy-, formyl- and keto-groups. Such types of compounds should be possible intermediates of cyclopentanone formation [33]. For example, Ordonsky et al. [35] detected in the reaction mixture the presence of cyclopentane diols and triol and on the bases of this fact they proposed that these compounds (not 4-HCP) are intermediates in cyclopentanone and cyclopentanol formation. Moreover, when under comparable conditions 4-HCP alone was hydrogenated the cumulative yield of cyclopentanone and cyclopentanol was maximal 73 mol% [14,36], what is significantly lower than in our experiments with furfuryl alcohol as a starting compound. It put some doubt if 4-HCP is the only intermediate (*) of FAL rearrangement [36], which is through 2-cyclopentenone converted to cyclopentanone (Scheme 2).

On the bases of presented results we suggest that beside 4-HCP also another type of intermediate is formed during rearrangement of FAL. In the presence of metal catalyst and sufficient hydrogen pressure the ionic reactive species formed from the initial elimination of a water molecule from FAL do not initiate FAL polymerization (reaction (2), Scheme 1). Probably these unstable ionic species are stabilized on the metal surface [14]. Since in the absence of hydrogen polymers are always formed, the metal surface must be covered by hydrogen atoms to avoid this reaction. Due to the rate of conversion of unstable ionic species to FAL polymers is suppressed (reaction (2)) and most probably the ring opening reaction [8] eventually partial hydrogenation of ring-opening species is promoted. A proposed pathway of conversion of the cationic intermediate formed by reaction (4) to a relatively stable and by GC detectable cyclopentenone (reaction (5)) involves nucleophilic conjugate 1, 4 addition with water leading to the ring opening reaction (Scheme 3). The presence of metal catalyst favours these reaction steps and stabilizes the formed cationic intermediate species. At sufficient hydrogen pressure hydrogen chemisorbed on the metal surface attacks the C=C bond of the chemisorbed intermediate X. Subsequently formed hydrogenated

species X1 after deprotonation and intramolecular condensation leads to β-hydroxy-cyclopentanone (species X2), which in acidic aqueous medium is unstable and rapidly dehydrated to cyclopentenone, observed in our experiments or in previous studies [36]. Also the participation of the metal catalyst on the cyclisation of formed reactive intermediate species cannot be excluded [37,38]. The proposed mechanism explains formation of cyclopentanone as the main intermediate product in the course of FAL rearrangement to cyclopentanone.

The rate of reaction (4), depending on the concentration of hydrogen ions can be influenced by adding acids or bases. However, these additives may also play an important role in determining the catalyst activity. On the contrary, sodium hydroxide, which has a negative impact on the conversion of FAL to main reaction products (Table 1, Run 9), the addition of an appropriate amount of acetic acid, has a positive effect on the yield of cyclopentanone (Table 1, Runs 6 and 8). For example, in Runs 5 and 6 the yield of cyclopentanone increased from 41.6 to 88.5 mol%. This increase was associated with the simultaneous decrease of THFA formation and the intermediate product, 2-cyclopentenone. Since cyclopentanone is not formed from THFA by consecutive reaction (Run 4) these results pointed out that the higher selectivity towards cyclopentanone in the presence of acetic acid is associated with the enhancement of the rate of reaction (4). Thus, at the unchanged rate of reaction (3) the added acetic acid increases the ratio of the rates of reaction (4) to (3) controlling the selectivity, and most probably increases also the rate of hydrogenation of intermediately formed 2-cyclopentenone to cyclopentanone (reaction (6)). As it is known, acidic conditions influence the mechanism of hydrogenation of unsaturated aldehydes and ketones [39,40]. Under acidic conditions is preferred the C=C versus C=O double bonds reduction. The hydrogenated product would desorb from the metal catalyst as the enol, which would then ketonize. Rapid ketonization of enol takes place by an attack of the acid. The formation of enolate intermediate with a copper catalyst involves also the mechanism proposed for the reduction of C=C double bonds in unsaturated cyclic ketones [41].

Fig. 3 shows the conversion of FAL and the distribution of the main reaction products as a function of reaction time at hydrogen pressure 0.8 MPa and very low concentration of the nickel catalyst (0.01 g catalyst per 1 g of FAL). In these experiments already during heating of the reactor (pressurized with hydrogen) to the reaction temperature (it lasts 12–15 min) a part of FAL is converted. At zero time, i.e. when the reaction temperature is reached, it is about 72%. However, an important fact is that under these conditions only less than 3 mol% of FAL is hydrogenated to THFA during 90 min of reaction. On the contrary, the desirable low reactivity of double bonds of furan ring, the C=C double bond of 2-cyclopentenone is completely converted with the prolongation of reaction time. After 90 min of reaction 95.7 mol% yield of cyclopentanone is achieved.

Besides the discussed influence of catalyst concentration and pressure of hydrogen on the rates of reactions (3) and (5) determining principally the selectivity towards cyclopentanone, a substantial impact on both reactions have also the type of heterogeneous metal catalyst. As we have proposed, the mechanism of FAL transformation in water involves participation of the metal catalyst on hydrogenation of the C=C bonds in the furan ring (reaction (3)) and in cyclopentenone (reaction (6)). The rate of reaction (4) determined mainly by the concentration of hydrogen ions is slightly dependent on the presence of metal catalyst. As is seen in Fig. 4, at the same reaction conditions and the weight ratio of catalyst to FAL, the effect of the type of metal catalyst on the distribution of reactions products formed either by rearrangement of the furan ring or its hydrogenation is relatively low. Using carbon supported Pt, Ru and Ni catalysts with 5 wt% of metal loading the yield of FAL rearranged products (cyclopentanone + cyclopentanol) is similar,

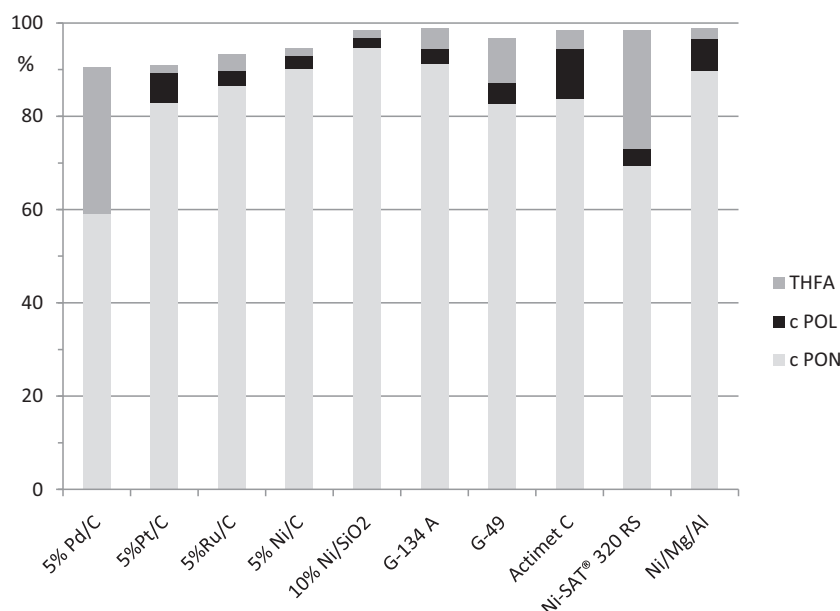


Fig. 4. The effect of various catalysts on products distribution. Conditions: 160 °C; weight ratio catalyst:FAL= 0.01; 2.5 MPa H₂.

about 90–93 mol%. Tetrahydrofurfuryl alcohol is produced only in 1.5–3.5 mol% yields. Very active and selective towards cyclopentanone are supported and bulk nickel based catalysts. In the presence of these catalysts only small part of FAL (less than 3 mol%) was hydrogenated to THFA. Less selective to cyclopentanone was found the Raney nickel Actimet C giving higher formation of cyclopentanol, probably as a result of consecutive hydrogenation of cyclopentanone. The activity and selectivity of nickel catalysts slightly increased when nickel was supported on silica or was incorporated into mixed Mg/Al oxides. The results in Fig. 4 confirmed that the tested nickel catalysts, including cheap commercial types, are highly active and selective to cyclopentanone.

Very high selectivities of FAL conversion to cyclopentanone + cyclopentanol obtained with supported and bulk types of Ni catalysts and very low production of THFA suggest that under reaction conditions hydrogenation of FAL to THFA is not influenced by the size of Ni particles of the used catalysts (the used catalysts had the size of nickel particles > 10 nm). This hydrogenation reaction should be enhanced over Ni/SiO₂ catalysts when nickel particles are very small (<4 nm) [28]. However, when nickel catalysts are used in an aqueous solution, one of the problems is metal leaching [42]. As was observed experimentally, the 10% Ni/SiO₂ catalyst separated by centrifugation, washed twice with 5 ml of water and reused gave almost complete conversion of FAL but the yield of cyclopentanone decreased by 8.9 mol%, under the same conditions as in Fig. 4. It should be caused by covering the metal sites with polymers of furfuryl alcohol and the leaching of nickel during the reaction. It was found that after one catalytic run less than 5 wt% of nickel was dissolved into aqueous reaction mixture. Using 5% Pd/C catalyst no leaching of palladium was observed.

Among the tested metal catalysts an exception is the palladium catalyst. Under comparable reaction and concentration conditions it is less selective to cyclopentanone and in its presence is substantially promoted the formation of THFA. However, when the concentration of palladium catalyst was decreased to a very low value (0.0025 g 5%Pd/C catalyst per 1 g FAL), hydrogenation of FAL to THFA was suppressed and the yield of cyclopentanone sharply increased to about 95% (Fig. 5). The effect of decreasing concentration of the palladium catalyst on the yield of cyclopentanone is similar as was observed for the nickel catalyst, but this effect was achieved at substantially lower concentrations of the palladium catalyst. According

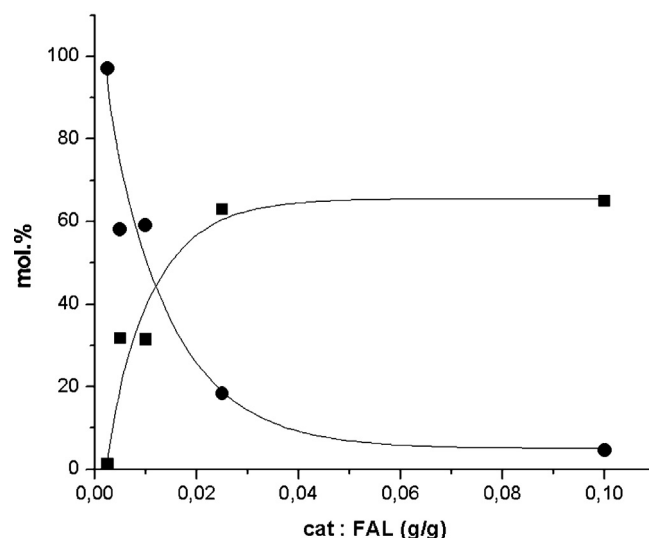


Fig. 5. The effect of 5%Pd/C catalyst concentration on distribution of cyclopentanone and tetrahydrofurfuryl alcohol. Conditions: 160 °C; weight ratio catalyst:FAL= 0.01; 2.5 MPa H₂.

to the proposed reaction mechanism at lower concentrations of the palladium catalyst the rate of reaction (3) is reduced without considerable influence on the rates of reactions (5) and (6). It suggests that the properties of palladium surface for the adsorption of furfuryl alcohol are different as for nickel. A significant role can play also co-adsorbed hydrogen which can be on the metal surfaces activated by homolytic or heterolytic dissociation. Therefore, at the given concentration of FAL and hydrogen in the liquid phase the rate of reaction (3) is determined by the strength of adsorption of furfuryl alcohol and hydrogen (and its activation by dissociation) on the metal surfaces, which should be also structure-sensitive.

4. Conclusions

The presented results pointed out that under reaction conditions, when mass-transfer effects are eliminated, the crucial role in the selective preparation of cyclopentanone from furfuryl alcohol

plays the concentration of metal catalyst and hydrogen dissolved in water, serving as a solvent. We devised the reaction mechanism of this reaction consisted of two simultaneous reaction pathways. The pathway leading to the production of cyclopentanone precursors involves an irreversible rearrangement reaction which is catalyzed by hydrogen ions created by self-dissociation of water. The second pathway, which negatively influences the selectivity towards cyclopentanone is the hydrogenation reaction of FAL to THFA, which is catalyzed by metals. Since the presence of metal catalyst is needed also for the hydrogenation of intermediate products of FAL rearrangement to cyclopentanone, by influencing both last mentioned reactions with catalyst concentration and hydrogen pressure we can control the selectivity to the desired product cyclopentanone. Very active and selective are nickel based catalysts, including cheap commercial types. In the presence of very low catalyst concentrations (0.0025–0.01 g catalyst per 1 g of FAL) and hydrogen pressure 0.8 MPa more than 95 mol% yields of cyclopentanone were achieved.

References

- [1] R. Xing, W. Qi, G.W. Huber, *Energy Environ. Sci.* 4 (2011) 2193–2205.
- [2] J.P. Lange, E. Van der Heide, J. Van Buijtenen, R. Price, *ChemSusChem* 5 (2012) 150–166.
- [3] I. Agirrezabel-Telleria, F. Hemmann, C. Jäger, P.L. Arias, E. Kemnitz, *J. Catal.* 305 (2013) 81–91.
- [4] H. Liu, H. Hu, M.S. Jahan, Y. Ni, *Bioresour. Technol.* 131 (2013) 315–320.
- [5] M.J.C. Molina, R. Mariscal, M. Ojeda, M. López Grandos, *Bioresour. Technol.* 126 (2012) 321–327.
- [6] I. Agirrezabel-Telleria, I. Gandarias, P.L. Arias, *Bioresour. Technol.* 143 (2013) 258–264.
- [7] W. De Jong, G. Marcotulio, *Int. J. Chem. React. Eng.* 8 (2010), Article A69.
- [8] Y. Nakagawa, M. Tamura, K. Tomishige, *ACS Catal.* 3 (2013) 2655–2668.
- [9] P. Gallezot, *Chem. Soc. Rev.* 41 (2012) 1538–1558.
- [10] N. Merat, C. Godawa, A. Gaset, *J. Chem. Technol. Biotechnol.* 48 (1990) 145–159.
- [11] X. Chen, W. Sun, N. Xiao, Y. Yan, S. Liu, *Chem. Eng. J.* 126 (2007) 5–11.
- [12] M.A. Tike, V.V. Mahajani, *Ind. Eng. Chem. Res.* 46 (2007) 3275–3282.
- [13] F.A. Khan, A. Vallat, G. Süß-Fink, *Catal. Comm.* 12 (2011) 1428–1431.
- [14] M. Hronec, K. Fulajtárová, T. Liptaj, *Appl. Catal. A: Gen.* 437–438 (2012) 104–111.
- [15] M. Hronec, K. Fulajtárová, T. Soták, *J. Ind. Eng. Chem.* 20 (2014) 650–655.
- [16] J. Scognamiglio, L. Jones, C.S. Letizia, A.M. Api, *Food Chem. Technol.* 50 (2012) S608–S612.
- [17] T. Takahashi, K. Ueno, T. Kai, *Microporous Mater.* 1 (1993) 323–327.
- [18] M. Hronec, K. Fulajtárová, T. Liptaj, M. Štolcová, N. Prónayová, T. Soták, *Biomass Bioenergy* (2013), submitted.
- [19] T. Akashi, S. Sato, R. Takahashi, T. Sodesawa, K. Inui, *Catal. Commun.* 4 (2003) 411–416.
- [20] H. Lerner, W. Hoelderich, M. Schwarzmann, US Patent 4822920 (1989) to BASF AG.
- [21] S. Liang, R. Fischer, F. Stein, J. Wulff-Doring, US Patent 6429339 (2002) to BASF AG.
- [22] P. Sudarsanam, L. Katta, G. Thimurthulu, B.M. Reddy, *J. Ind. Eng. Chem.* 19 (2013) 1517–1524.
- [23] K.A. Dubkov, G.I. Panov, E.V. Starokon, V.N. Parmon, *React. Kinet. Catal. Lett.* 77 (2002) 197–205.
- [24] J.H. Teles, M. Chabanas, T. Genger, B. Rossler, EP Patent 2155642 (2007) to BASF AG.
- [25] S. Li, L. Guo, Ch. Zhu, Y. Lu, *Int. J. Hydrogen Energy* 38 (2013) 9688–9700.
- [26] M. Hronec, K. Fulajtárová, *Catal. Commun.* 24 (2012) 100–104.
- [27] A.V. Bandura, S.N. Lvov, *J. Phys. Chem. Ref. Data* 35 (2006) 15–30.
- [28] Y. Nakagawa, H. Nakazawa, H. Watanabe, K. Tomishige, *ChemCatChem* 4 (2012) 1791–1798.
- [29] G. Piancatelli, A. Scettri, G. David, M.D' Auria, *Tetrahedron* 34 (1978) 2775–2778.
- [30] C. Piutti, F. Quartieri, *Molecules* 18 (2013) 12290–12312.
- [31] E. Holz, V. Köhler, B. Appel, P. Langer, *Eur. J. Org. Chem.* (2005) 532–542.
- [32] S. Caddick, S. Cheung, V.E. Doyle, L.M. Frost, M.G. Soscia, V.M. Delisser, M.R.V. Williams, Z.C. Etheridge, S. Khan, P.B. Hitchcock, G. Pairaudau, S. Vile, *Tetrahedron* 57 (2001) 6295–6303.
- [33] S.P. Roche, D.J. Aitken, *Eur. J. Org. Chem.* (2010) 5339–5358.
- [34] M. Minai, US Patent 4970345 (1990) to Sumitomo Chem. Co.
- [35] V.V. Ordonsky, J.C. Schouten, J. van der Schaaf, T.A. Nijhuis, *Appl. Catal. A: Gen.* 451 (2013) 6–13.
- [36] Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao, J. Xu, *Green Chem.* 15 (2013) 1932–1940.
- [37] I.J.S. Fairlamb, *Annu. Rep. Prog. Chem. B: Org. Chem.* 103 (2007) 68–89.
- [38] Ch.J. Li, *Chem. Rev.* 105 (2005) 3095–3165.
- [39] R.L. Augustine, A.D. Broom, *J. Org. Chem.* 25 (1960) 802–804.
- [40] A. Rossin, G. Kovacs, G. Ujaque, A. Lledós, F. Joó, *Organometallics* 25 (2006) 5010–5023.
- [41] V. Jurkauskas, J.P. Sadighi, S.L. Buchwald, *Org. Lett.* 5 (2003) 2417–2420.
- [42] Y. Nakagawa, K. Tomishige, *Catal. Commun.* 12 (2010) 154–156.